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Life cycle impact analysis of cadmium in CdTe PV production

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Abstract

This paper describes the material flows and emissions in all the life stages of CdTe PV modules, from extracting refining and purifying raw materials through the production, use, and disposal or recycling of the modules. The prime focus is on cadmium flows and cadmium emissions into the environment. This assessment also compares the cadmium environmental inventories in CdTe PV modules with those of Ni–Cd batteries and of coal fuel in power plants. Previous studies are reviewed and their findings assessed in light of new data.
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Keywords: Cadmium emissions; Photovoltaics; Solar cells; Cadmium telluride; Life cycle analysis; Emissions allocation

Contents

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1. Introduction

Life Cycle Assessment (LCA) involves analyzing the inventory of material and energy flows in and out of a product, and assessing the impacts of such flows. Previous applications of LCA to photovoltaics focused on determining energy payback time (EPT) and reductions in carbon-dioxide emissions [1–4]. Kato et al. [4] emphasized the need for further studying the environmental aspects of CdTe photovoltaics, including decommissioning and recycling of end-of-life CdTe modules. The current study characterizes material flows and emissions in thin-film CdTe PV modules, from acquiring the raw material through their production, use, and disposal or recycling. It describes in detail the flows of the major photovoltaic compound (CdTe); other materials in the PV module (e.g. glass, EVA, metal contacts) are generic to all technologies and, therefore, are not discussed. In addition to reviewing the published literature, I examined the environmental reports of several primary producers of the metal. This assessment also discusses the allocation of Cd emissions in co-production of metals, and makes a comparative evaluation of CdTe with other uses of cadmium.

Below I describe the material flows and emissions in the following phases of the life of CdTe modules: (1) mining of ores, (2) smelting/refining of Cd and Te, (3) purification of Cd and Te, (4) production of CdTe, (5) manufacture of CdTe PV modules, and, (6) disposal of spent modules.

2. Production of cadmium and telluride

CdTe is manufactured from pure Cd and Te, both of which are byproducts of smelting prime metals (e.g. Cu, Zn, Pb, and Au). Cadmium is generated as a byproduct of smelting zinc ores (~80%), lead ores (~20%), and, to lesser degree, of copper ores. Tellurium is a byproduct of copper refining. Cadmium is used primarily in Ni–Cd batteries. Its previous uses in anticorrosive plating, pigments, and stabilizers were drastically curtailed. Cd also is used in the control rods of nuclear reactors. Tellurium is a rare metal used in manufacturing photosensitive materials and catalysts.

2.1. Cadmium production

Cadmium minerals are not found alone in commercial deposits. The major cadmium-bearing mineral is sphalerite (ZnS), present in both zinc and lead ores. Cadmium occurs in the crystal structure of zinc sulfides; only rarely does it form (in combination with sphalerite) its own isostructural sulfide—greenockite. The cadmium content in the various ores are as follows: sphalerite, 0.0001–0.2%; greenockite, 77.8%; chalcopyrite, 0.4–110 ppm; marcasite, 0.3–50 ppm; arsenopyrite, ~5 ppm; galena, 10–3000 ppm; and, pyrite, 0.06–42 ppm [5]. Table 1 shows the cadmium content in other mineral feedstocks.

2.1.1. Mining of zinc and lead-ores

Zinc is found in the earth's crust primarily as zinc sulfide (ZnS). Zinc ores contain 3% to 11% zinc, along with cadmium, copper, lead, silver and iron, and small amounts of gold, germanium, indium, and thallium. Lead-rich ores also contain zinc, copper, and silver in sulfide forms. In underground mines, the ore is excavated by drilling machines, processed through a primary crusher, and then conveyed to

Table 1
Cadmium content in mineral feedstocks

Material	Concentration range (ppm)	US median (ppm)
Zn ores	0.1–2000	220
Zn ore concentrates	3000–5000	5000
Copper ore concentrates	30–1200	NA
Iron ore	0.12–0.30	NA
Coal	0.4–10	0.5
Heavy oil	0.01–0.10	–
Phosphate ore	0.25–80	–

the surface. In open-pit mines, the ore is loosened and pulverized by explosives, scooped up by mechanical equipment, and transported to the concentrator.

The concentration of zinc in the recovered ore (called beneficiating) is done by crushing, grinding, and flotation processes (Fig. 1). Standard crushers, screens, and rod- and ball-mills reduce the ore to powder of 50–210 microns. The particles are separated from the gangue and concentrated in a liquid medium by gravitation and/or selective flotation, followed by cleaning, thickening, and filtering [6a]. At this stage, organic xanthate and a froth-promoter, usually pine oil, are added. The mixture is treated in banks of flotation machines—shallow tanks in which a rotating impeller disperses fine bubbles of air. When the pH and reagents have been adjusted, the air bubbles carry the sulfide minerals to the surface of the pulp for removal. The proper combination of reagents causes the selective flotation of zinc sulfides, lead sulfides, and copper sulfides, and rejects the iron sulfides and rock to tailings. The metal concentrates are dewatered, dried, and shipped to metallurgical plants, with each sulfide being sent to the appropriate smelter; the water is recycled to the mill. The waste, called tailings, is discharged in tailing ponds. Zinc concentrates contain about 85% zinc sulfide and 8–10% iron sulfide. The cadmium content of the zinc concentrate is around 0.3% to 0.5% [7]. Limited information exists on the cadmium content of tailings. Measurements of soil contamination in a mine site at Brooksville, Maine, which ceased operations in 1972, show cadmium in the soil, tailings, and waste rock ranging from undetected levels to 150 ppm [8]. Data from a lead–zinc mine in Maarmorilik, Greenland, showed 57 ppm of Cd in the tailings in 1978, but, by 1985, this had fallen to 14 ppm (Table 2); more recent

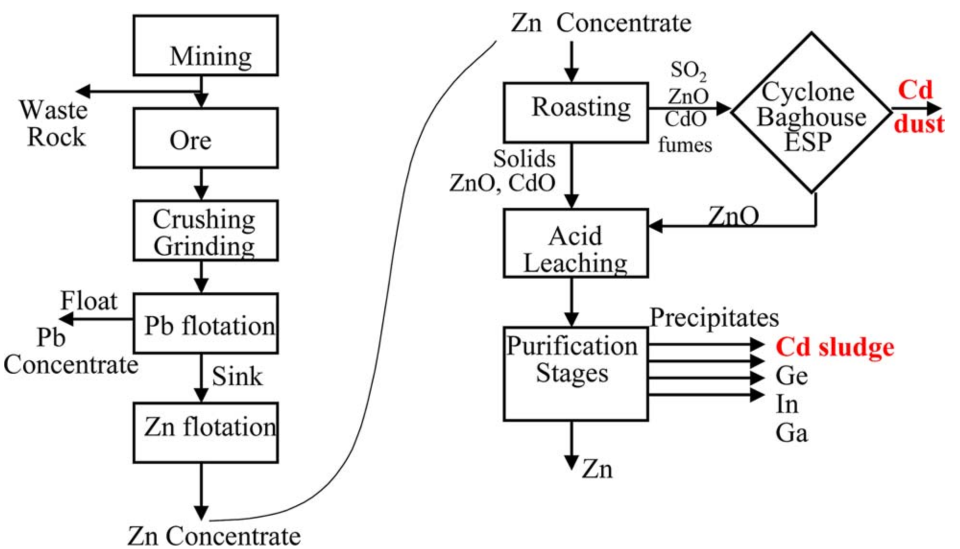


Fig. 1. Cd Flows in Zn mining and refining.

data were not found. Assuming that the initial Cd concentration in the ores was 220 ppm, this reflects a loss of 6% in the tailings. This value is the middle point of the range given in a 1994 report of the US Bureau of Mines [7]. According to Liewellyn [7], between 90% and 98% of the cadmium present in zinc ores is recovered in the mining and beneficiting stages, and the balance of cadmium remains in the mine tailings.

Similarly to zinc ores, lead-bearing ores are processed by crushing, screening and milling, to reduce the ore to powder. These activities, if not adequately controlled, could generate significant levels of dust (e.g. 3 kg/ton of mined ore), ranging from 0.003 kg to 27 kg per ton of ore [9]. However, ASARCO and Cominco, two major metal producers, report that implement controls which minimize dust emisisons. All of the mining, crushing, and grinding takes place underground and wet scrubbers and dry cyclones are utilized to collect the dust. Cominco uses a wet grinding process resulting in a slurry from which, reportedly, there are essentially no dust emisions [6b]. Therefore, the low limit of the range (i.e. 0.003 kg/ton ore) was used in our analysis.

In both zinc and lead mining operations, in addition to intrinsic waste, mining generates an assortment of wastes, including liquids from maintaining equipment in mills, and from mobile equipment at mines. Major North American producers have waste-reduction and residuals-management programs. Large open-pit mines create large volumes of waste oil, which is recycled on-site. Waste oil from Canadian operations is collected and recycled off-site. In some other locations, waste oil is reused by cement plants as a source of energy.

2.1.2. Zinc and lead smelting/refining

The zinc and lead concentrates are transferred to smelters/refiners to produce the primary metals; sulfuric acid and other metals are frequent byproducts from most smelters (Fig. 2). In addition to Zn, the mines in the United States also produce 100% of the Cd, Ge, In, and Th, 10% of Ga, 6% of Pb, 4% of Ag and 3% of Au used in the country [10,11]. Also, integrated zinc–lead smelters/refiners recycle significant volumes of solid- and liquid-wastes (lead acid batteries, waste grease, drums, plastic pails, tires, conveyor belting, wood, office paper, cardboard, and many other end-of-life-consumer goods). For example, 22,000 tones of lead acid batteries and other battery materials were reprocessed at the Teck Cominco Trail smelter in 2002.

Table 2
Data from the Black Angel lead–zinc mine, Greenland*

Metal	Average content in ore (%)	Content in tailings	
		1978	1985
Zn	12.3	1.1%	0.23%
Pb	4	0.44%	0.15%
Cd	?	57 ppm	14 ppm

*Source: http://www.geus.dk/minex/go02.pdf.

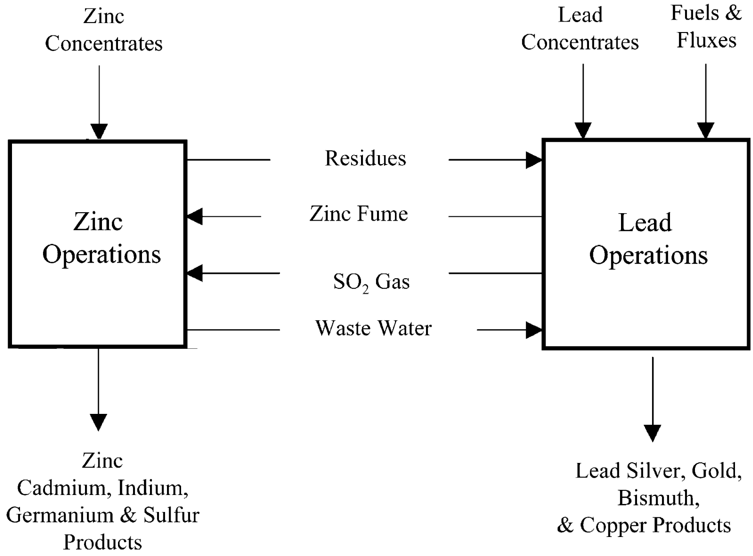


Fig. 2. General process schematic for zinc/lead smelting (*Source*: http://www.teck.com/environment/articles.htm).

2.1.2.1 Zinc production. Zinc can be refined by either pyrometallurgical or hydrometallurgical treatment of its concentrates (Fig. 3). There are four primary zinc-smelting operations in the United States. Three of them utilize electrolytic technology, and one uses an electrothermal process [6]. Older roast/retort smelters are no longer employed in North America and Northern Europe. The electrolytic zinc process consists of five main operations, roasting, leaching, purification, electrodeposition and melting/casting (Fig. 3). These are described below:

(i) Oxidizing roast at high temperature removes sulfur and converts the zinc, iron, cadmium, and other metals to oxides. The concentrates are fed to fluidized-bed furnaces where they react with oxygen. The product, calcine, which mainly is zinc oxide with small amounts of iron, cadmium, and other metals, is pneumatically transported to storage bins before the next phase of treatment. The roaster gases, containing sulfur dioxide, are separated from the calcine and cooled in a waste-heat boiler, to recover heat and generate steam. They are usually treated to recover mercury, while the collected particulates are processed to recover cadmium. Sulfur dioxide is used to produce sulfuric acid.

(ii) Calcine and spent electrolytes from the subsequent electrolytic process are leached in sulfuric acid. This process, in one or two steps, dissolves the zinc to make a solution of zinc sulfate and other acid-soluble metals. Iron is precipitated and filtered from the process as a residue. Depending on the ore, the residue may also contain lead, copper, silver, and gold. The leachate is sent to the purification section.

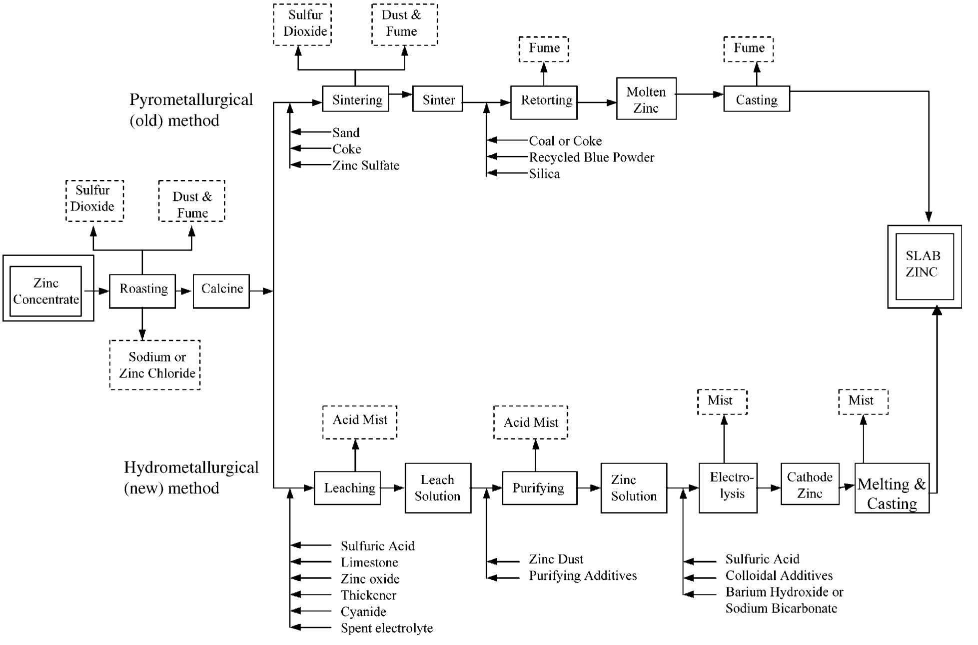


Fig. 3. Generalized process flow for primary zinc smelting [6a].

(iii) In subsequent purification, iron and various other valuable metals (e.g. copper, cobalt, nickel, cadmium, germanium, indium, and gallium) are removed, usually in three stages. After the third stage, the solution, which contains zinc sulfate and residues of copper and cadmium, is pumped to the electrowinning stations. The cadmium extracted at this step is formed into briquettes that then are melted. This refining results in metallurgical grade (99.95% pure) cadmium, which is cast and cut into sticks.

(iv) Recovery of metallic zinc from the sulfate solution is accomplished by electrowinning. Zinc is reduced from a solute into a metallic form by electrodeposition on aluminum sheet cathodes. Every 36 h or so, the Zn-covered cathodes are removed and the pure zinc layer covering them is stripped off and fed into induction furnaces. Also sulfuric acid is regenerated in this stage.

(v) The final steps in zinc production are melting, casting, and alloying. The zinc stripped off from the cathodes is melted, and cast into ingots, slabs, or larger blocks of slab ready for delivery to customers [6,14a].

In addition to cadmium, zinc smelting also produces (as byproducts) other photovoltaic materials (i.e. Ge, In, and Ga). Because economic growth has steadily increased the demand for zinc for decades, impure cadmium is produced, regardless of its use. Before cadmium production started in the United States in 1907, about 85% of the Cd content of the zinc concentrates was lost in roasting the concentrate,

and in the fractional distillation of Zn metal [7]. The feed material for producing cadmium consists of residues from the electrolytic production of zinc, and of fume and dust, collected in baghouses from emissions during pyrometallurgical processing [6].

Primary zinc production produces air emissions, process wastes, and solid-phase wastes. The zinc roasting process primarily emits sulfur dioxide. These emissions often are recovered on-site in sulfuric-acid production plants. Zinc roasters also generate particulates containing cadmium, lead, and other metals. The particulate emission streams are controlled with cyclones and electrostatic precipitators (ESPs), and the particulates collected in the control equipment constitute hazardous waste. As discussed later, this waste comprises the feed to the cadmium-production plant.

Wastewater produced from leaching, purification and electrowinning usually is treated and re-used or discharged.

Solid wastes include slurries from the sulfuric-acid plant, sludge from the electrolytic cells and copper cakes, and the byproducts of zinc production from the purification cells which contain cadmium, germanium, indium, and other metals. Much of the waste is RCRA[1] hazardous waste. Copper cakes are captured and sold to copper processing plants. Purification byproducts and other solid wastes are recycled or stockpiled until they can be economically used. Table 3 shows the US EPA's estimates of particulate emissions for US plants; I estimated their cadmium content based on a typical concentration of Cd in Zn concentrate (e.g. 0.5%).

Berdowski et al. [13a] reported on the emissions from zinc-smelting operations in other countries; these are summarized in Table 4. Cd emissions vary widely depending on the ore used and the abatement measures applied. For electrolytic production, emission factors of 0.5 g Cd/ton Zn were reported in 1992 for the Netherlands, 2 g Cd/ton Zn in 1991 for Germany, and a range of 0.4–20 was reported for 1980–1992 for Poland. More recent data show 0.2 g Cd per ton of Zn product for North European countries [12a,12b,13a]. This corresponds to about 40 g per ton of Cd produced.

Slightly higher emissions are reported from one of the world's largest integrated zinc- and lead-smelting and refining complexes, the Teck Cominco complex in Trail, British Columbia, Canada [14b]. In addition to zinc and lead, 18 other products are formed including silver, gold, indium, germanium, bismuth, copper products; and sulfur compounds (e.g. ammonium sulfate fertilizer, sulfuric acid, liquid sulfur dioxide and elemental sulfur). The reported cadmium releases from all operations at Trail in 2002 were 95 kg in air and 208 kg in water; they correspond, per ton of metals produced, to 0.27 g of Cd air emissions, and 0.59 g of water discharges (Table 5). Only total emissions from all operations were reported; the contribution of the cadmium plant to these emissions is difficult to determine because feeds and residuals were transferred between plants in the same facility. Also, the

[1] The RCRA, the Resource Conservation and Recovery Act, characterizes what constitutes hazardous waste by either listing or leaching tests.

Table 3
Particulate emission factors in zinc smelting by thermal (old) and electrolytic (new) methods

Process	Uncontrolled emissions (kg/ton of zinc ore)	Post-control emissions (kg/ton of zinc concentrate)	Estimated[a] Cd emissions (kg/ton of zinc concentrate)
Roasting			
Multiple hearth	113	ND	ND
Suspension	1000	4	0.02
Fluidized bed	1083	ND	ND
Sinter plant			
Uncontrolled	62.5	NA	NA
With cyclone[b]	NA	24.1	0.14
With cyclone and ESP[b]	NA	8.25	0.05
Vertical retort	7.15	ND	ND
Electric retort (electrothermic process)	10.0	ND	ND
Electrolytic process	3.3	ND	ND

ND, not detected.
[a] Cadmium content in particulates is estimated assuming a zinc/cadmium ratio of 200 (0.5% Cd).
[b] Data not necessarily compatible with uncontrolled emissions.

Trail smelting facility processes metal scrap and other waste in addition to Zn and Pb ores. These data show a continuing improvement from 1989 to 2002. The actual emissions of Cd into the air declined by 84% between 1999 and 2002 (Table 5). Releases in the water within this period remained approximately the same.

The shift to electrolytic processing of zinc ore was a great technological advance that drastically reduced cadmium emissions because it eliminated the sintering step in zinc refining, and thus, much of the particulates burden. The Cd emissions in previous generation smelters amounted to 100 g of Cd per ton of Zn produced (Table 6), whereas those from current roast/leach/electrolytic European plants have fallen to 0.2 g of Cd per ton of Zn. In the past, high cadmium concentrations were found in the vicinity of lead and zinc smelters. Also, the early practice of roasting zinc sulfide and discharging the SO_2 into the atmosphere was replaced by

Table 4
Emission factors for primary zinc production (g/ton product) [13a]

Compound	Germany 1991		Poland 1980–1992		Netherlands 1992	Europe 2002	
	Thermal	Electrolytic	Thermal	Electrolytic	Electrolytic	Thermal	Electrolytic
Cadmium	100	2	13	0.4–29	0.5	50[a]	0.2
Lead	450	1	31–1000[b]	2.3–467	–	1900	–
Mercury	5–50	–	–	–	–	8	–
Zinc	–	–	420–3800	47–1320	120	16,000	6

[a] With vertical retort and limited abatement: 200 g/Mg product; with imperial smelting furnace: 50 g/Mg product.
[b] Limited abatement.

Table 5
Production and emissions at the Trail smelter and refineries, British Columbia, Canada [14][a]

	1998	1999	2000	2001	2002
Annual production					
Zinc (tonnes)	274,300	288,700	272,900	168,100	269,000
Lead (tonnes)	63,900	75,700	91,300	55,200	80,700
Cadmium (tonnes)		1400	1400	1400	1400
Specialty metals (tonnes)		28	28	28	28
Silver ('000 ounces)	12,215	11,382	12,212	9,182	17,690
(tonnes)	463	431	463	348	670
Gold ('000 ounces)	86	46	56	48	127
(tonnes)	3	2	2	2	5
Fertilizer (tonnes)	273,000	240,700	220,300	167,500	225,000
Cd releases to air from all operations					
(kg/year)		600	250	100	95
(g of Cd/ton metal products)		1.64	0.69	0.45	0.27
Cd releases to water from all operations					
(kg/year)		208	290	170	208
(g of Cd/ton metal products)		0.57	0.79	0.76	0.59

[a] *Source*: Teck Cominco; http://www.teck.com/operations/trail/index.htm (For specialty metals and cadmium only 2002 production levels were reported; we assumed that production in 1999–2001 was at the same levels as 2002.

converting the gas to sulfuric acid. The remaining particulate emissions are controlled with ESPs and bag-houses having efficiencies of 98–99.5%.

2.1.2.2 Lead production. Lead comes to smelters in the form of lead-sulfide concentrate and automotive battery scrap. They are processed by a combination of pyrometallurgical and hydrometallurgical operations. The feedstocks are heated in a furnace with oxygen, fluxing and fueling agents. Smelting creates impure lead bullion, slag, and gaseous emissions, primarily SO_2. Energy is recovered from the hot-emissions by passing the gasses through a heat exchanger, while an electrostatic precipitator removes the particles. The SO_2 emissions then are processed into sulfur products (e.g. sulfuric acid and liquid sulfur dioxide) [14a].

Table 6
Cadmium emissions from old and new zinc-production processes

Process	Cadmium emissions	
	g Cd/ton Zn	(% Cd loss)
Roast/leach/electrowinning process	0.2	0.008
Roast/blast furnace smelting (replaced in Canada and Europe)	50	2
Roast/blast furnace smelting (not in use any more)	100	4

The molten slag is transferred to a slag-fuming furnace to remove zinc, mainly in the form of a zinc-oxide fume. The fume is processed in the leaching plants in zinc operations to extract more zinc. The remaining "ferrous granules" (black sand-like slag) is sold to cement manufacturers.

The lead bullion is processed through a dosing plant to remove copper and other impurities. The remaining bullion is purified in the lead refinery by melting and electrolytic processing, and cast into the finished product. Byproducts of the refining process include silver, gold, arsenic, antimony, and bismuth. Emissions of cadmium from all sources range from 0.6 g/ton product for plants with cyclones and ESPs, to 22 g/ton product for plants with limited emissions abatement (Table 7).

The lead smelters also produce significant quantities of silver, gold, bismuth, and copper products (Table 5 and Fig. 2). These plants are designed to treat a wide range of feed materials including lead concentrates, various residues from the zinc plants, recycled lead battery scrap, and scrap copper [14a].

2.1.3. Production of cadmium in zinc–lead smelters/refiners

Cadmium recovery plants use as their raw materials cadmium residues from the leaching/electrolytic zinc production, particulates from roaster furnaces collected with electrostatic precipitators (ESPs), and recycled zinc metal which contains cadmium. In addition, they process particulates collected from lead smelting furnaces.

2.1.3.1 Cadmium production from zinc electrolyte purification residue. The cadmium sponge, a purification product from precipitating zinc sulfate solution with zinc dust at the zinc smelter, is 99.5% pure cadmium. This sponge is transferred to a cadmium recovery facility and is oxidized in steam for two days or so. Cadmium oxide, the product, is leached with spent cadmium electrolyte and sulfuric acid to produce a new recharged electrolyte. Impurities are precipitated with a strong oxidizing agent. The wastes are refined for other uses or stockpiled, usually until a use can be found for them. Non-corrosive anodes are used during electrowinning.

Table 7
Emission factors for primary lead production (g/ton product) [13b]

	Sweden 1992		Poland 1980–1992			Germany 1999	Europe 1950–1985
Abatement level	Limited	Improved	Limited	Improved	Unabated	Unknown	Unknown
Compound							
Arsenic	3	0.2	16–43	–	–	3	300
Cadmium	3	0.6	10–22	–	–	6	10
Copper	10	4	10	7	–	–	–
Lead	400	200	560–1200	–	–	400	3000
Mercury	–	–	–	–	–	–	3
Zinc	50	20	110	–	680	–	110

Additives (often animal glue) are used to enhance the smoothness of the resulting cadmium cathode. The cathodes are removed about every 24 h and are rinsed and stripped. The stripped cadmium is melted under flux or resin and cast into shapes.

In a slightly different route, purification residues from the oxide and the sulfide-leaching processes are further leached with sulfuric acid and filtered through three stages to remove zinc, copper, and thallium before recovering the dissolved cadmium. Cadmium can be further purified with vacuum distillation to 99.9999% purity [14].

2.1.3.2 Cadmium production from lead smelter emissions. The fumes and dusts of lead smelters are concentrated to 8–60% cadmium by weight and shipped to the cadmium recovery plant where they are reacted with sulfuric acid. The resulting calcined cadmium sulfate and impurities are roasted and then leached with water to dissolve the cadmium. The cadmium sulfate solution is first filtered to remove the lead sulfate, which is recycled to the lead smelter, and then further purified by electrolytic separation.

The resulting electrolyte is 99.995% pure. The cadmium is melted under flux or resin and cast into shapes. The spent electrolyte is recycled at the cadmium recovery plant. When excessive amounts of impurities accumulate in the spent electrolyte, the solution is recycled to another use or neutralized and discarded.

The total loss in emissions and residues at cadmium plants is about 5% [7]. Thus, about 95% of Cd from Cd concentrates is converted in metallurgical grade (99.99%) metal, which is used in all current applications, except for semiconductor CdTe and CdHgTe. High purity (i.e. 99.999%–99.9999%) Cd (and Te) powders are produced by electrolytic purification and subsequent melting and atomization or by vacuum-distillation followed by zone refining.

2.2. Tellurium production

Tellurium minerals are not found alone in commercial deposits. Tellurium is a rare metal that can be extracted as byproduct of processing copper, lead, gold, and bismuth ores. In 1982, about 90% of tellurium was recovered from the slimes formed during the electrolytic refining of copper [15]. Copper is mined from a variety of ores containing copper in the form of mineral compounds with sulfur, iron, arsenic, and tin. Copper concentrates of about 30% Cu are produced at the mine sites via crushing, grinding, and flotation. They are transferred to smelters where they are processed in furnaces to yield "mate" containing about 65% copper. The iron in this mate is oxidized to produce "blister" copper of 97% to 98.5% purity that can be further refined hydrometallurgically or by a combination of pyrometallurgical and hydrometallurgical separation. Impurities in blister copper include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, tin, and zinc. In pyrometallurgical separations, air is bubbled through the molten mixture to remove the impurities by oxidation. The fire-refined copper is cast into anodes for further purification by electrolytic refining. In electrolytic refining, the impurities are separated by electrolysis in a solution containing copper sulfate and sulfuric acid. The copper anode dissolves and metallic impurities pre-

cipitate forming a sludge. The copper collected on the cathode is about 99.95% pure [16].

The slimes contain copper, tellurium, selenium, and other metals. Copper typically is removed by oxidative pressure-leaching with dilute sulfuric acid at 80–160 °C. This completely extracts the Cu, and removes 50–80% of the Te according to one source [17] or more than 90% according to another [18]. The range of Te extraction is wide because its concentration in slimes varies significantly. Tellurium is recovered from solution by cementation with copper. Copper telluride is leached with caustic soda and air to produce a sodium telluride solution. The latter is used as the feed for producing commercial grade Te metal or TeO_2. As discussed in Section 4, both of these forms can be used in CdTe formation for PV.

Crushing and grinding of ores in copper mines generates dust emissions of the same levels as those in mining zinc- and lead-ores (discussed in Section 2.1.1).

Emissions generated from primary copper smelters include sulfur dioxide and particulates from the roasters, smelting furnace, and converters. Copper and iron oxides are the primary constituents of the particulate matter; other constituents include the oxides of arsenic, antimony, cadmium, lead, mercury, and zinc. There are eight copper smelters in the United States. Sulfur dioxide is recovered in the form of sulfuric acid in all but one of these smelters. Particulate emissions are treated in ESPs or combination spray/ESP systems with efficiencies of 95–99%. The emissions from copper smelting can vary widely depending on the ore used and the abatement measures applied. I found no explicit quantification of cadmium emissions in copper smelting in the literature. Indirect estimates can be made from comparing the Cd concentrations in copper and lead smelters; Table 8 shows those compiled by Ayres and Simonis [19]. According to these numbers, copper smelters would produce 3.2 to 5 times lower Cd emissions than lead smelters. These emissions are primarily related to pyrometallurgical operations. Emissions in hydrometallurgical/electrolytic plants are likely to be negligible unless the sulfuric-acid tanks are open to the atmosphere.

Table 8
Uncontrolled emissions from metallurgical operations [19]

Metal	Steel and foundries (ppm)	Smelt/refine copper (ppm)	Smelt/refine lead (ppm)
Arsenic	15.2	8000 (refinery 800–900)	
Cadmium	3.5–4.0	350–650	1750–2100
Chromium	6.5–7.0	–	–
Copper	17.5–22.5	2500–5000	–
Mercury	–	26 air 1 water	9 air 0.5 water
Lead	200–300	2000–5000 (refinery 25)	20,000–23,000
Zinc	27–370	9000–11,000	500–1000

2.3. Purification of cadmium and tellurium

Metallurgical grade (i.e. 99.99% pure) metal is used in all current applications except for semiconductor materials (e.g. CdTe and CdHgTe) that require higher purity. Teck Cominco reports that all the cadmium they produce is ultra-pure grade (i.e. 99.9999%, called six 9s). Purification residues from their leaching plants undergo additional leaching with sulfuric acid and are filtered though three stages to remove zinc, copper, and thallium. The final step is vacuum-distillation [11].

High purity Cd and Te powders from other manufacturers are produced by electrolytic purification and subsequent melting and atomization (Fig. 4), or by vacuum distillation. Both methods are proprietary and information about emissions is not published. According to industry sources, electrolytic purification does not produce any emissions and all waste is recycled. The melting and atomization steps needed to form the powder produce about 2% emissions that are captured by HEPA filters [20]. The efficiency of HEPA filters in collecting particulates of mean diameter of 0. 3 μm is 99.97%.

Zone-refining involves four steps during which the concentrations of impurities are reduced below levels detected by standard analytical techniques [21–25].

2.4. Production of CdTe from cadmium and tellurium

Currently, high purity Cd and Te are used in synthesizing high purity (five 9s to six 9s) CdTe for PV cells. CdTe is produced from Cd and Te powder via pro-

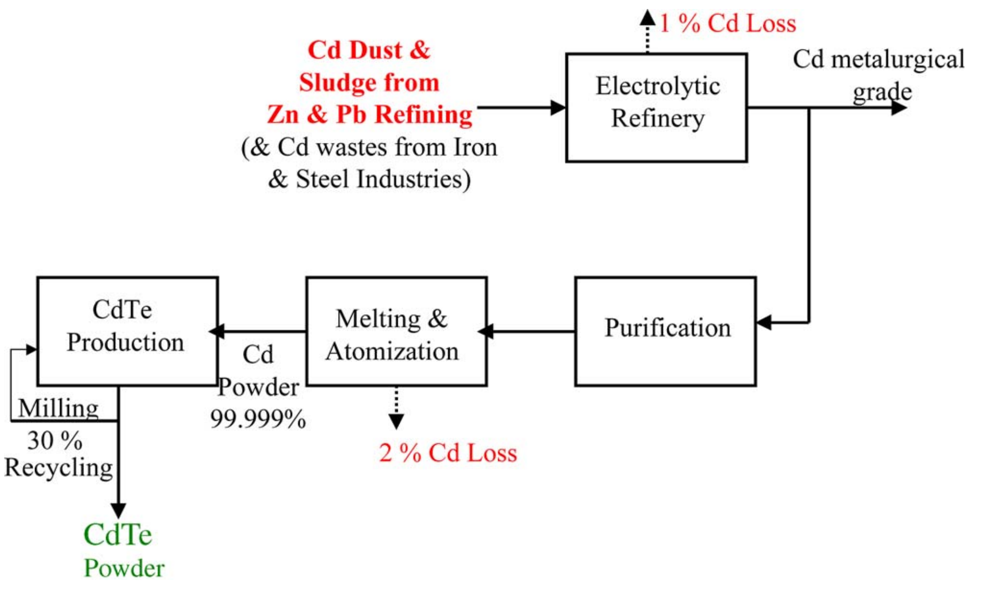


Fig. 4. Cd Flows from Cd Concentrates to CdTe.

prietary methods. CdTe is produced in small amounts for detectors and photovoltaics. Production is limited and the volumes produced are not published.

Reportedly, 100% of the feedstock is used and there are no quantifiable emissions during CdTe formation. The electrolytic purification does not produce any emissions and all waste is recycled. The melting and atomization steps necessary to form the powder emit about 2% of the feedstock which are captured by HEPA filters [20]. Milling produces some undesirably large particles, which are recycled into the process.

3. Allocation of emissions

Cadmium is a byproduct of zinc, lead, and copper production, and is collected from the emissions and waste streams of these major metals. Tellurium is a byproduct of copper production, and is also collected from waste streams. In obtaining cadmium from zinc ores, the emissions from the production of zinc are captured and used for this purpose. Should we allocate these cadmium emissions to the production of zinc, or to the production of cadmium and other byproducts? The recovery of low-value byproducts and waste for use as industrial raw materials is referred as "waste mining" [46]. Assuming a fixed level of demand for the prime metal (copper or zinc), the choice is between leaving the minor metal in gangue, slag, or dust, or recovering it for use. Recovery is encouraged for precious metals (e.g. gold and silver) that have value, and their applications are environmentally harmless. The value of recovering Cd is debatable. Cadmium used in pesticides and pigment stabilizers is dissipated and may not alter the environmental fate of cadmium waste from mining in any other way than by diluting it. On the other hand, semiconductors and batteries are products that are both collectable and recyclable (i.e. non-dissipative uses).

The problem of allocation in Life Cycle Assessment for joint production is a fundamental one [26]. The International Standard Organization (ISO) specifies a procedure (ISO 14041) for deciding such allocation [27]. It entails the following steps: (1) Allocation should be avoided, whenever possible, by dividing the process into subprocesses, and including the additional functions related to co-products. (2) Where allocation cannot be avoided, the system's inputs and outputs should be partitioned to reflect the underlying physical relationships between them (i.e. they must mirror the way the inputs and outputs are altered by quantitative changes in the products or functions). (3) Where physical relationships alone cannot be established or used as a basis for allocation, inputs should be allocated between the products in proportion to the products' economic values.

According to the first step of the ISO procedure, I considered separately zinc and cadmium production (Figs. 1 and 4 correspondingly). Thus, the zinc cycle starts with mining the Zn ores and ends with generating the Zn product, whereas the cadmium cycle starts with creating the Cd-bearing waste and emissions from zinc operations, and includes the steps related to the collection, concentration, and purification of waste/emissions. This approach avoids the allocation of co-products,

Table 9
Emissions allocation based on material output from Zn-ore

Metal	Typical grade in ore (ppm)	Emissions allocation (%)
Zn	40,000	99.44
Cd	200	0.50
Ge	20	0.05
In	4	0.01

Table 10
Emissions allocation based on the economic value of products from Zn-ore

Metal	Typical grade in ore (ppm)	Prices 1998[a] ($/kg)	Primary production (10^3 ton/year)	Production economic value (10^6 $/year)	Emissions' allocation (%)
Zn	40,000	1.1	7000	7700	97.82
Cd	200	0.6	20	46	0.58
Ge	20	1700	0.05	70	0.89
In	4	306	0.2	56	0.71
Total				7872	100

[a] US Geological Survey, Commodity Statistics and Information; 1998 Prices for 99.99% Cu; 99.99% Cd; 99.9999% Ge; 99.97% In. http://minerals.usgs.gov/minerals/pubs/metal_prices/.

in agreement with well-accepted LCA practices [28]. Its justification is that zinc production alone determines the amount of cadmium produced; demand for it has zero effect on the quantity of cadmium generated.

However, for sensitivity analyses, I also estimated allocation of emissions according to the ISO's steps 2 and 3. Following step 2, the allocation is based on mass output, and, according to step 3, it is determined by the economic value of the produced metals. Tables 9 and 10 show these allocations. For determining the production economic value for each metal, we use the price (value) of the pure metal, although subprocess 1 produces waste streams, thereby slightly overestimating the allocation of emission to Cd and the other byproducts. The allocation in Table 10 is based on 1998 prices (the most recent year in which data for all metals were published by the USGS). Based on typical grade in Zn ore (40,000 ppm Zn, and 200 Cd), and current (June 27, 2003) prices of 0.78 $/lb for zinc, and 1.0 $/kg for cadmium, the economic value ratio of Zn-to-Cd is 168.

4. Manufacturing of CdTe photovoltaics

There are two leading methods of making CdTe/CdS thin films; electrodeposition of CdTe combined with chemical surface deposition of CdS, and high-rate vapor transport of the two compounds.

4.1. Electrodeposition and chemical surface deposition

In electrodeposition, a CdTe thin film is deposited on a substrate attached to the cathode of an electrolytic system using an aqueous solution of cadmium sulfate ($CdSO_4$) or cadmium chloride ($CdCl_2$), and tellurium dioxide (TeO_2). During deposition, the concentration of Cd ions is maintained by periodically adding solid precursor to the solution. The concentration of Te ions is kept constant by using a Te anode in addition to the graphite inert anode. The concentration of Cd is maintained between 0.1 and 1.2 M, and that of Te at 10^{-4} M, at a pH of 2–3. The electrolytic bath is replenished continuously and less than 1% of Cd and Te are wasted since deposition only occurs on surfaces held at the cathode.

Electrodeposition of CdTe usually is accompanied by chemical-bath deposition (CBD) of CdS, a process that, until recently, had a very low (e.g. $<5\%$) material utilization. Precipitated Cd solids from CBD and residuals on the walls of the bath had to be recycled by converting them to Cd solids suitable for re-use in CdS deposition [29]. In a former commercial facility in Fairfield, CA, all aqueous waste containing Cd and Te compounds, from rinsing, plate stripping, and ion-exchange regeneration, were treated by a two-stage precipitation/ion exchange system that precipitated Cd compounds and, after filtration, removed the Cd solids, producing solutions with Cd levels as low as 10 ppm. In the second stage, the ion-exchange system removed Cd down to the 1–10 ppb range, leaving a liquid that could be disposed of or recycled, via the process deionizing water plant. Precipitated Cd solids were recycled by conversion to Cd salts [29]. In the laboratory, 99.999% cadmium has been recovered from CBD wastes by a combination of leaching and electrodeposition [30].

The volume of waste from CBD that needs to be recycled was reduced remarkably in a new development on CdS deposition. McCandless and Shafarman [31] obtained material utilization of more than 90% by applying the liquid precursors directly on a heated substrate (chemical surface deposition, CSD), instead of dipping it in a heated chemical bath. This already has become the baseline process at the Institute of Energy Conversion, University of Delaware, and will be the basis of our emissions' analysis. The liquid used is an aqueous solution of $CdSO_4$, $CS(NH_2)_2$, and $NH_4(OH)$, with Cd^{++} solution concentrations between 1.5 and 3 mM.

In summary, both electrodeposition of CdTe and chemical surface deposition of CdS are about 90% efficient, and, after recycling of the residuals, not more than 1% of the cadmium and tellurium used in the facility would be lost in the form of very dilute liquid and waste streams. Moskowitz et al. [32] estimated that for a 10 MW/year facility, using 1156 kg of $CdSO_4$ and 880 kg of TeO_2 to deposit a 3 μm CdTe layer, these losses correspond, respectively, to 11.6 kg (6.2 kg of Cd), and 8.8 kg (6.4 kg of Te).

4.2. Vapor transport deposition

In vapor transport deposition, CdS and CdTe are deposited from the compounds in powder form after vaporization in a close-spaced reactor. The current material utilization rates range from 35% to 70%, but higher utilization rates are expected in optimized scaled-up production. Most of the unused vapors condense on the reactor's walls or rollers from where they are removed periodically. The deposits are either disposed of or recycled; recycling is both feasible and economic, and will be practiced in large-scale production. Less than 1% of the vapors are carried in the exhaust stream. The vapor and dust emissions are collected at 99.97% efficiencies[2] using HEPA filters in the exhaust, and vacuum-HEPA tools during maintenance. The HEPA filters are disposed of as hazardous waste when they are saturated. In $CdCl_2$ systems, the material is deposited from liquid solutions at 80–90% utilization efficiency. These systems are totally contained and all residuals are recycled. Under optimized conditions in a large facility, about 10% of the feedstock materials may eventually be disposed in the form of cadmium-contaminated solid wastes. For a 10 MW/year facility using 3720 kg of CdTe, 200 kg of CdS, and 480 kg of $CdCl_2$, this loss, respectively, amounts to 372, 20, and 48 kg of solid waste, containing a total of 850 kg of Cd. The above estimates are based on currently attainable 10% electrical conversion efficiency, 10% area loss, 83% production yield and 70% material utilization rates for depositing 3 μm CdTe and 0.15 μm CdS layers. Future generation CdTe solar cells may be thinner and production yields may be higher than those we assumed.

The two leading methods of making CdTe thin films—electrodeposition and vapor transport—use cadmium very efficiently. About 1% is wasted in the former process, and about 10–30% in the latter. In both processes, the cadmium is collected and is safely disposed of or recycled. The controlled (with HEPA filters) vapor emissions into the atmosphere amount to 3 g of Cd per ton of Cd used.

5. Operation of CdTe PV modules

5.1. Routine releases

Thin-film α-Si, CdTe, and CIGS solar cells are durable and do not produce any emissions during extreme conditions of accelerated aging in thermal cycles from +80 to −80 °C [33]. Every PV generation, regardless of technology, is a zero-emissions process. The thin CdTe/CdS layers are encapsulated between sheets of glass or plastic. Unless the module is ground to a fine dust, dust particles cannot be generated. The melting point of CdTe is 1041 °C, and evaporation starts at 1050 °C. Sublimation occurs at lower temperatures, but the vapor pressure of CdTe at 800 °C is only 2.5 torr (0.003 atm). The melting point of CdS is 1750 °C and its vapor pressure due to sublimation is only 0.1 torr at 800 °C. Therefore, it is

[2] For particles of 0.3 μm or larger.

impossible for any vapors or dust to be emitted when using PV modules under normal conditions.

5.2. Potential accidental releases

The only pathways by which people might be exposed to PV compounds from a finished module are by accidentally ingesting flakes or dust particles, or inhaling dust and fumes. Steinberger [34a] addressed the potential of Cd leaching out by rain from broken or degraded CdTe modules at the GSF Institute of Chemical Ecology in Germany. He concluded that CdTe releases are unlikely to occur during accidental breakage. The only scenario of potential exposure is if a fire consumes the PV module and releases cadmium from the material into the air.

In fully developed house fires, flame temperatures can reach 800–1000 °C. In industrial fires where other fuels are present, higher flame temperatures could occur. Steinberger [34b] conducted thermogravimetric analyses of *pure* CdTe and reported that the material, exposed to air, remains stable until about 1050 °C, whereas it started to evaporate at around 900 °C under non-oxidizing conditions

Table 11
Results of fire simulating tests on CdTe PV modules

T (°C)	500	760	900	1000	1100
Heating duration (min)	60	30	30	120	240
Cd weight loss (%)	0.2	0.6	0.4	0.5	0.4

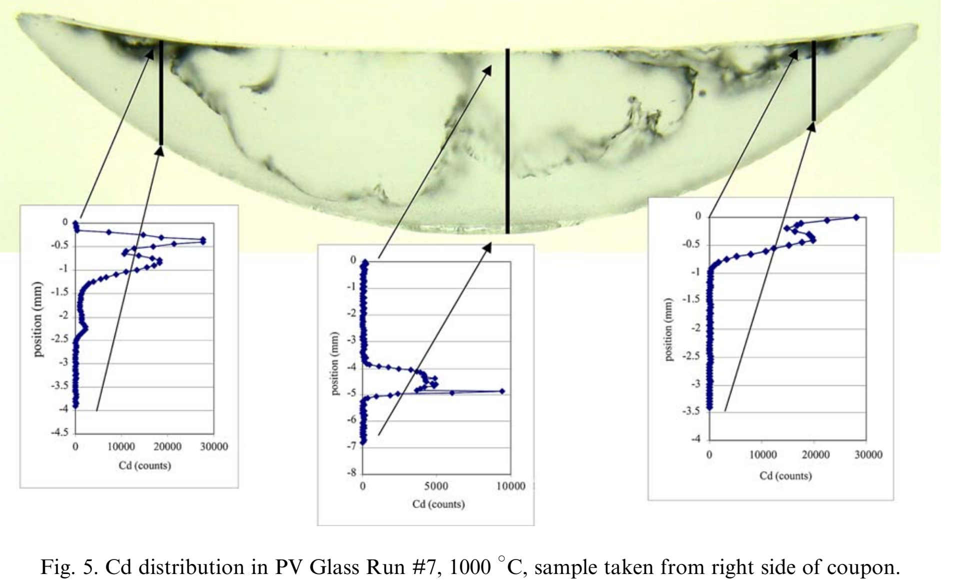


Fig. 5. Cd distribution in PV Glass Run #7, 1000 °C, sample taken from right side of coupon.

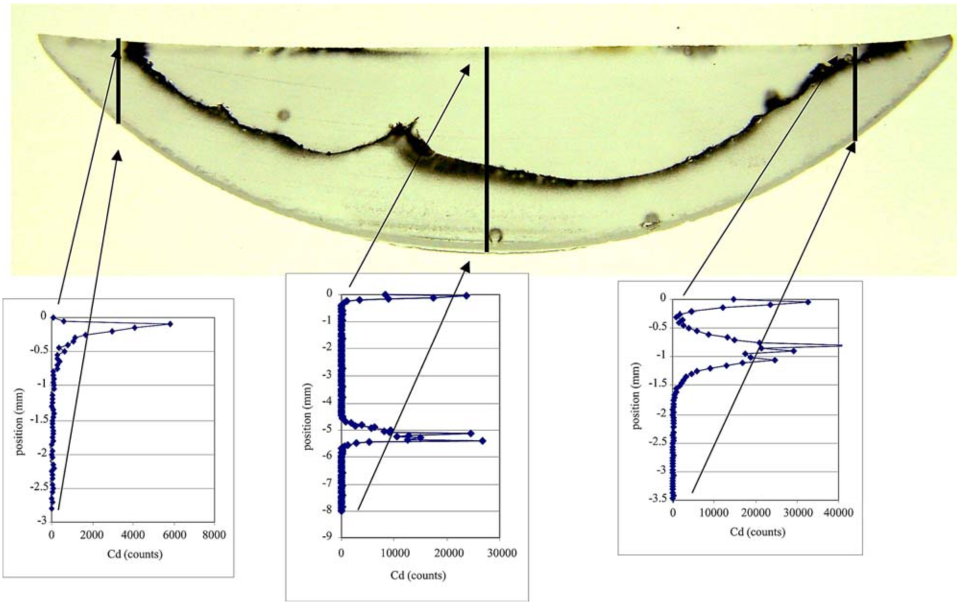


Fig. 6. Cd distribution in PV Glass Run #7, 1000 °C, sample taken from center of coupon.

(lack of air). I note that oxidizing conditions are the only realistic ones for high temperature tests, since lack of oxygen would extinguish the fire.

The fire effect on glass-to-glass encapsulated CdTe modules was recently investigated at BNL. In our studies, 1.5″ by 12″ pieces (coupons) cut from PV modules were exposed to temperatures of 760–1100 °C, for 30-min to 3 h, following standard protocols by the American Society for Testing and Materials (ASTM) and the Underwriters Laboratories (UL). In these experiments, CdTe was captured in the molten glass and was not released into the environment. Only 0.4% to 0.6% of the Cd content of the coupons was released during these tests (Table 11). This Cd release likely occurred from the open perimeter of the coupon before the two sheets of glass melted together, and is expected to be negligible in whole modules where the ratio of perimeter to surface area is 13.5 times smaller. The dissolution of Cd in the molten glass was confirmed with high-energy synchrotron x-ray microprobe analysis; two samples of these analyses are shown in Figs. 5 and 6. Details of this analysis can be found elsewhere [35].

6. End-of-life disposal or recycling

PV modules are expected to last 25–30 years. Should the modules at the end of their useful life end up in municipal landfills or incinerators, potentially heavy metals could be released into the environment. CdTe PV modules that pass leaching criteria for non-hazardous waste could be disposed of in landfills, according to

current laws. The leachability of metals in landfills currently is characterized by elution tests such as the US-EPA Toxicity Characterization Leachate Profile (TCLP), and the German DEV S4 (Deutsches Einheitsverfahren). Both assume a worst-case scenario. In these tests, small pieces (<1 cm^2) of broken modules are suspended and rotated in an eluent for 24 h. The metals present in the eluent then are measured and compared with limits prescribed by each testing protocol. If the metals' concentration exceeds the limits, the modules are demonstrating the metals' leachability and may need to be recycled or disposed of in a hazardous-waste landfill; if the metals are not leaching above the limits, the modules can be disposed of in a commercial landfill. Some early CdTe modules failed the TCLP and the DEV tests [36]. Cunningham [37] reported that the Apollo modules produced by BP Solar pass the TCLP. Environmental regulations can increase the cost and complexity of dealing with end-of-life PV modules. If they were classified as "hazardous" according to Federal or State criteria, then special requirements for material handling, disposal, record keeping, and reporting would escalate the cost of decommissioning. Previous studies showed that PV recycling is technologically and economically feasible, but not without careful forethought [38,39]. A recycling program was outlined, based on current collection- and recycling-infrastructure, and on emerging recycling technologies. Metals from used solar-panels in large centralized applications can be reclaimed in metal-smelting facilities, which use glass as a fluxing agent and recover most of the metals by incorporating them into their product streams. In dispersed operations, small quantities and high transportation costs make this option expensive. For these operations, as well as small-scale recycling, hydrometallurgical separations are economical [40]. These processes start with physically separating module frames, junction boxes and wires; then, the modules are fragmented, and the metals are stripped in successive steps of chemical dissolution, mechanical separation, and precipitation or electrodeposition. Another option is to leave the glass substrate intact (and the SnO_2-conducting layer), potentially allowing their re-use for PV deposition. At the end, the mounts, glass, EVA, and a large fraction of metals are recovered (e.g. 80–96% of Te, Se, Pb). The remaining metals (e.g. Cd, Te, Sn, Ni, Al, Cu) are contained in a sludge, which must be disposed of, or further recycled. The estimated total cost, excluding transportation, is approximately 4–5 ¢/W. The estimated total cost of recycling in smelters thin-film PV modules or scrap from large installations is about 5 ¢/W; from dispersed installations, it is about 12 ¢/W [39,41]. INMETCO recovers 100% of Cd from Ni–Cd batteries. Such extensive separation could be expected from CdTe PV modules.

A valid assumption is that CdTe PV modules will be either recycled or properly disposed off at the end of their useful life; therefore atmospheric emissions during/after decommissioning will be zero. Even if pieces of modules inadvertently make it to a municipal waste incinerator, cadmium will dissolve in the molten glass and would become part of the solid waste.

7. Total atmospheric emissions

Our estimates of atmospheric cadmium emissions during all the phases of the life of CdTe PV modules are shown in Tables 12–14. Table 12 shows the most likely case (Reference case). The results in Table 13 reflect the allocation of Cd emissions during mining, smelting and refining to Cd as well as Zn production. Allocations based on the mass output and on the economic value of the products were very similar and produced the same results. Table 14 shows estimated emissions assuming worst conditions, i.e. mining/smelting/refining by old methods (outside North America, West Europe and Japan), reduced effectiveness of HEPA filters, and reduced PV module life expectancy.

Our reference estimate of total air emissions is 0.02 g Cd/GWh of electricity produced, which is 25 times lower than the estimate (i.e. 0.5 g Cd/GWh) reported by Alsema [43]. The main contributor to Cd air emission in the later assessment was PV utilization, under the assumption of Cd loss during fires. As discussed earlier, extensive experimental tests proved that Cd is not emitted during fires. Also, our assessment uses more recent data for determining emissions during mining, smelting/refining, and decommissioning of end-of-life products. As discussed in Section 2.1.2 the Cd atmospheric emissions in North America and European smelters have been drastically reduced within the last 10 years.

Table 12
Reference case—atmospheric Cd emissions from the life-cycle of CdTe PV modules

Process	Air emissions (g Cd/ton Cd[a])	Allocation		Air emissions	
		(%)	(g Cd/ton Cd)	(mg Cd/m^2)	(mg Cd/GWh)
1. Mining of Zn ores	2.7	0	0	0.00000	0.00
2. Zn smelting/refining	40	0	0	0	0.00
3. Cd purification	6	100	6	0.042	7.79
4. CdTe production	6	100	6	0.042	7.79
5. CdTe PV manufacturing	3	100	3	0.021	3.90
6. CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/recycling	0	100	0	0	0.00
Total emissions			15.00	0.11	19.48

Assumptions:
1. All emissions during mining/smelting/refining are assigned to Zn production.
2. The ratio of Zn to Cd content of Zn ores is 200.
3. The mean concentration of Cd in Zn ores is 220 ppm.
4. HEPA filters have a 99.97% effectiveness in collecting submicron size particulates in PV manufacturing exhaust streams.
5. Emissions per module area and energy output are based on:
   7 g Cd/m^2 module
   10% Electric conversion PV efficiency
   Average US insolation (1800 kWh/m^2/year)
   30 years PV module life expectancy, thus
   1 kg Cd produces 0.77 GWh over its life-time in PV.

[a] ton of Cd used in manufacturing.

Table 13
Sensitivity case 1—atmospheric Cd emissions from the life-cycle of CdTe PV modules (Allocation of emissions to co-production of Zn, Cd, Ge and In)

	Air emissions (g Cd/ton Cd[a])	Allocation (%)	Air emissions		
			(g Cd/ton Cd)	(mg Cd/m^2)	(mg Cd/GWh)
1. Mining of Zn ores	2.7	0.58	0.0157	0.0001	0.02
2. Zn smelting/refining	40	0.58	0.2320	0.0016	0.30
3. Cd purification	6	100	6	0.042	7.79
4. CdTe production	6	100	6	0.042	7.79
5. CdTe PV manufacturing	3	100	3	0.021	3.90
6. CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/recycling	0	100	0	0	0.00
Total emissions			15.25	0.11	19.80

Assumptions:
1. Mining of zinc ores produces 30 g of dust per ton of ore.
2. Smelting/refining of Zn produces 0.2 g of Cd per ton of Zn production
3. The ratio of Zn to Cd content of Zn ores is 200.
4. The mean concentration of Cd in Zn ores is 220 ppm.
5. HEPA filters have a 99.97% effectiveness in collecting submicron size particulates in PV manufacturing exhaust streams.
6. Emissions per module area and energy output are based on:
   7 g Cd/m^2 module
   10% electric conversion PV efficiency
   Average US insolation (1800 kWh/m^2/year)
   30 years PV module life expectancy, thus
   1 kg Cd produces 0.77 GWh over its life-time in PV

[a] ton of Cd used in manufacturing.

8. Comparisons with other energy technologies

The total Cd use in the United States in 1997 was 2600 tons; globally, it is approximately 20,000 tons per year. Cadmium is employed primarily (~65%) in nickel–cadmium rechargeable batteries, paint pigments (~17%), plastic stabilizers (~10%), for metal plating (~5%), and metal solders (~2%). Using only 1.5–3% of the nation's consumption of cadmium in manufacturing CdTe solar cells (i.e. 40–80 ton/year) would generate over 1 GW of new PV per year. I note that the total current PV capacity in the United States is only 0.3 GW and is projected to grow (under optimistic assumptions) to about 3.2 GW/year by 2020. Even envisioning an order-of-magnitude higher PV production (e.g. 32 GW/year) would require only about a sixth to a third of the current US Cd consumption. New solar energy at such very large scales would significantly change the mix of electricity sources in the US and abroad, preventing carbon dioxide and other emissions.

It is interesting to compare Cd flows in CdTe PV with those in Ni–Cd batteries and coal-burning power plants.

Table 14
Sensitivity case 2—atmospheric Cd emissions from the life-cycle of CdTe PV modules (*Worst cases* in mining/smelting/refining, PV use and PV manufacturing)

	Air emissions (g Cd/ton Cd[a])	Allocation (%)	Air emissions		
			(g Cd/ton Cd)	(mg Cd/m^2)	(mg Cd/ GWh)
1. Mining of Zn ores	27	0.58	0.1566	0.0011	0.29
2. Zn smelting/refining	1000	0.58	5.8000	0.0406	10.76
3. Cd purification	12	100	12	0.084	22.26
4. CdTe production	12	100	12	0.084	22.26
5. CdTe PV manufacturing	6	100	6	0.042	8.57
6. Fires during CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/recycling	0	100	0	0	0.00
Total emissions			35.96	0.25	66.71

Assumptions:
1. Mining of zinc ores produces 30 g of dust per ton of ore.
2. Smelting/refining of Zn produces 50 g of Cd per ton of Zn production (old, thermal method).
3. The ratio of Zn to Cd content of Zn ores is 200.
4. The mean concentration of Cd in Zn ores is 220 ppm.
5. HEPA filters effectiveness in PV manufacturing reduced by a factor of 2 to 99.93%.
6. Emissions per module area and energy output are based on:
 7 g Cd/m^2 module
 10% electric conversion PV efficiency
 Average US insolation (1800 kWh/m^2/year)
 20 years PV module life expectancy
 thus, 1 kg Cd produces 0.51 GWh over its life-time in PV

[a] ton of Cd used in manufacturing.

8.1. Ni–Cd batteries

As discussed in Section 3, using Cd in Ni–Cd batteries is widely considered to be the least dissipative of its current major uses, and, therefore, the friendliest to the environment. This is because Ni–Cd batteries can be collected and their Cd content effectively recycled. For example, Ni–Cd batteries collected in the United States are recycled at the International Metals Reclamation Company (INMETCO) facility in Ellwood City, Pennsylvania. The plant relies on High Temperature Metal Recovery and produces cadmium at a 99.95% purity level that is used in new Ni–Cd rechargeable batteries.

However, the problem with small consumer type batteries is collecting them. In contrast, PV modules by virtue of their size would be more difficult to "escape" collection and end inadvertently in a landfill or municipal-waste incineration plant.

Cadmium in Ni–Cd batteries is in the form of Cd and $Cd(OH)_2$, materials which are less stable and more soluble than CdTe (Table 15). The latter is less soluble and possibly less toxic than its parent compound. CdTe modules are very well sealed and Cd cannot be released during normal operation, or even during fires in residential roofs.

Table 15
Characteristics of Cd compounds used in Ni–Cd batteries and CdTe PV

Compound	$T_{melting}$ (°C)	$T_{boiling}$ (°C)	Solubility (g/100 cc)	Carcinogen
Cd	321	765	Insoluble	Yes
$Cd(OH)_2$	300	–	2.6×10^{-4}	Yes
CdTe	1041	–	Insoluble	?
CdS	1750	–	1×10^{-4}	Likely
$CdCl_2$	568	960	140	Yes

The amount of Cd in a Ni–Cd batteries ranges from 3.2 to 21 g depending on the battery's size (Table 16). The amount of Cd in CdTe solar cells is very small, and could be reduced even further as the cells become thinner; a Ni–Cd C-size flashlight battery contains more Cd than a square meter of today's CdTe PV module. The Ni–Cd battery industry estimates that an AA or C size Ni–Cd battery can be re-charged 700–1200 times over its life [42]. Under this assumption, a battery would produce an average of 0.046 kWh per g of its weight, which corresponds to 0.306 kWh per g of Cd contained in the battery. This is a 2500 times lower efficiency in using Cd than in a CdTe PV module.

8.2. Coal-burning power plants

Other investigators have compared potential Cd emissions from operation of photovoltaics and from the operation of coal-burning power plants [43]. First, I note that such comparisons are erroneous since they compare potential *accidental* emissions from PV systems to *routine (unavoidable)* emissions from modern coal-fired plants. Second, assuming a 10% or higher release rate for Cd from CdTe PV, was recently found to be invalid. Our quantification of such releases for glass–glass encapsulated modules, under a wide range of fire conditions, showed that Cd diffuses in the molten glass and is not released in the environment.

Coal-fired power plants routinely generate Cd during operation in contrast to PV which can not generate emissions during normal use. According to data from the US Electric Power Research Institute (EPRI), under the best/optimized operational and maintenance conditions, burning coal for electricity releases into the air generates a *minimum* of 2 g of Cd/GWh (assuming well-maintained electrostatic precipitators or baghouses operating at 98.6% efficiency, and median concentration

Table 16
Cd Content in CdTe PV and NiCd batteries

	g/unit	mg/kWh (kg/Gwh)
PV CdTe	7 g/m^2	1.3
NiCd battery—AA size	3.2	3265
NiCd battery—C size	10.5	3265
NiCd battery—C size	21	3265

of Cd in US coal of 0.5 ppm)[44]. It is noted, that although very high effectiveness is expected for ESPs operating in North American, Western European and Japanese power plants, ESPs are much less effective, if they are installed at all, in developing, coal-burning countries. In addition, 140 g/GWh of Cd inevitably collects as fine dust in boilers, baghouses, and ESPs, thereby posing occupational health- and environmental-hazards. Furthermore, a typical US coal-power plant emits per GWh about 1000 tons of CO_2, 8 tons of SO_2, 3 tons of NO_x, and 0.4 tons particulates.

9. A fundamental question: what happens to cadmium if it is not used?

As discussed in Section 2, cadmium is mainly a byproduct of zinc smelting, and its supply is proportional to the supply of zinc. When the market does not absorb all the Cd generated by metal smelters, the residues from which Cd is recovered are either stockpiled for future use, cemented and buried, or disposed of [45].

Therefore, there are two strategies for reducing the environmental releases of cadmium. The first is to cut back on producing and consuming zinc, and the second is to use cadmium in ways that prevent its flow to the environment. It is important to distinguish the uses of cadmium in terms of its dissipation (i.e. the degree of inevitable spreading into the environment), and cadmium-bearing waste streams in terms of their physical and chemical forms as they affect mobility and toxicity. Cadmium in fertilizers is inherently dissipative, whereas Cd in Ni/Cd batteries and photovoltaics is not, since the products can be collected at the end of their useful life. Although some dissipative uses of zinc (e.g. in pigments, chemicals) might be curtailed, it would be hard to find replacements for its major uses (e.g. steel corrosion protection, die casting, brass and bronze products). The most obvious way to cut down on the production of zinc, and subsequently cadmium, is to encourage recovery and recycling of secondary zinc, especially from galvanized metal sheet and zinc-based cells [46].

Regarding safe to the environment uses, major European studies have pointed out that using cadmium in Ni–Cd batteries is such a use, provided that they can be remanufactured or recycled effectively [19,46]. The Rhine Basin, one of the most industrialized regions of the world, experienced cadmium contamination in the 1980s from using phosphate fertilizers, and from the emissions of zinc smelters, steel production plants and coal-fired power plants. The largest contributor to cadmium contamination in the Rhine Basin was likely the production of cadmium, and the production, use, and disposal of cadmium products (Fig. 7) [19]. Cadmium metal, some of which is produced at the region's zinc refineries and some of which is imported, is the input to plants that manufacture the four major cadmium-containing products; pigments (mostly for plastics), nickel–cadmium (Ni–Cd) batteries, plates (for surface protection of steel and other metals), and stabilizers (in PVC plastic). Emissions of cadmium occurred for each of these manufacturing sectors. The Rhine Region study of industrial metabolism provided valuable insights into the various flows and environmental interactions of metals in the region. One

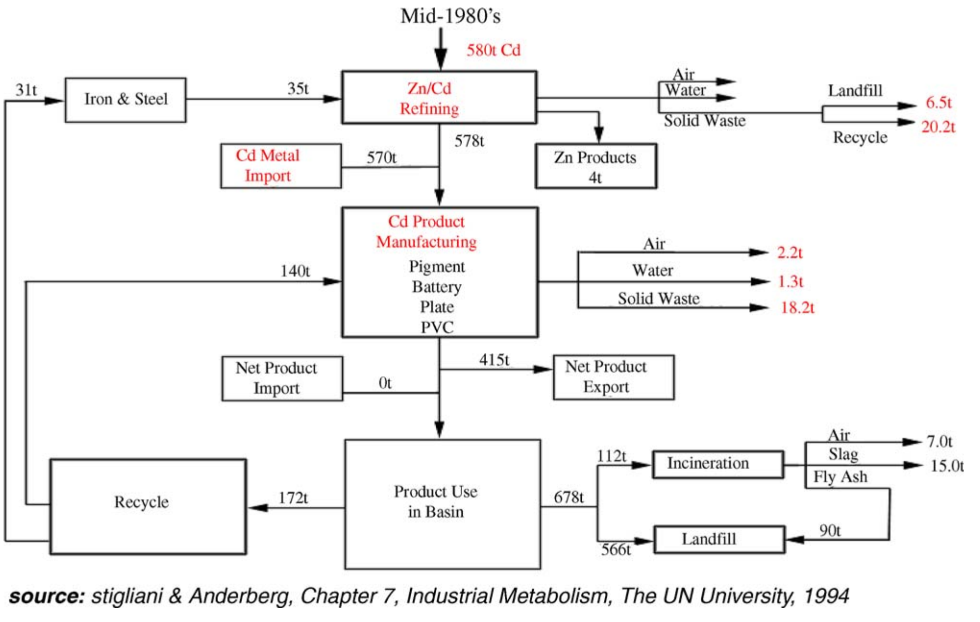


Fig. 7. Cd flow in the Rhine Basin, 1980s [19].

of the scenarios explored is banning the dissipative uses of cadmium in the region and recycling 50% of the Ni–Cd batteries (Fig. 8). The following conclusion refers to this scenario [19]:

> "So, the ultimate effect of banning Cd products and recycling 50% of disposed consumer batteries may be to shift the pollution load from the product disposal phase to the Zn/Cd production phase. This does not imply that banning Cd-containing products is not a wise strategy; rather, it indicates that if such a ban were to be implemented, special provisions would have to be made for the safe handling of surplus Cd wastes generated at the Zn refineries. *One possible option would be to allow the production and use of Cd-containing products with inherently low availability for leaching*. The other option, depositing the Cd-containing wastes in safely contained landfills, has other risks."

Some argued that using Cd to construct statues might be a good option [47]. However, it may not be a value-adding one. I concluded that using Cd in CdTe PV modules is more environmentally friendly than any other current approach. Such use is non-dissipative and the product is very stable. Compared to Ni–Cd batteries, CdTe photovoltaics use CdTe, a more stable compound than either Cd or $Cd(OH)_2$. CdTe modules are very well sealed and Cd cannot be released during normal operation, or even during accidental fires or breakage of PV modules. In addition, PV modules are much bulkier and, therefore, are much easier to collect

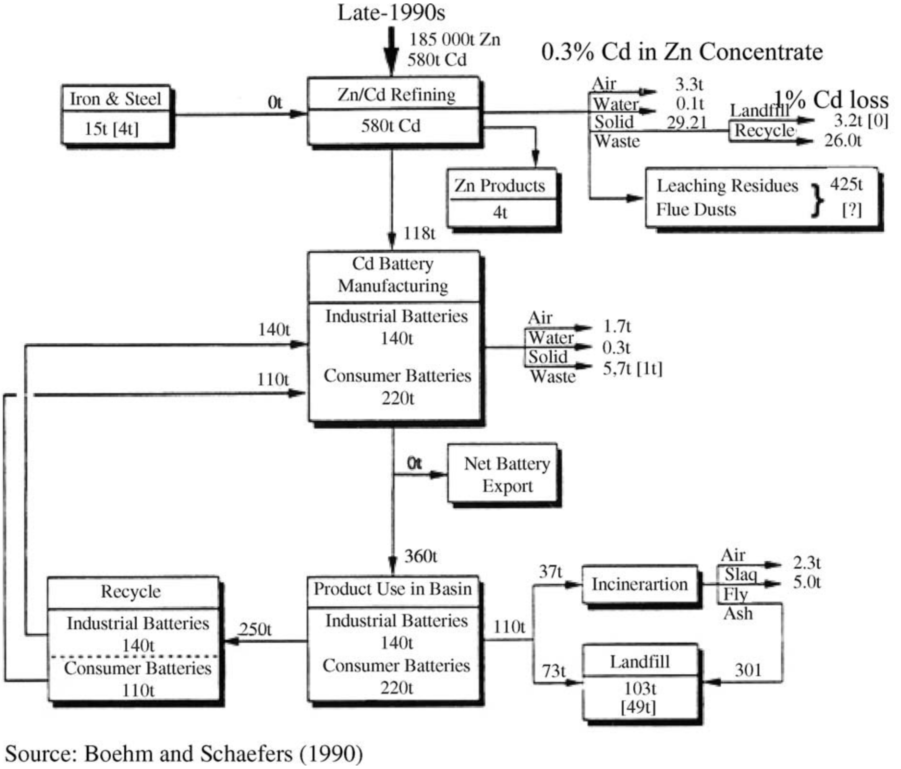


Fig. 8. Cd flow in the Rhine Basin, 1990s [19].

for recycling or safe disposal than consumer batteries. Using Cd in CdTe PV modules effectively isolates and sequesters this compound.

10. Conclusion

The flows and emissions of cadmium in CdTe PV modules were studied in detail for all the different phases of large-scale implementation of this technology. The following conclusions were derived for the different phases of the life of CdTe PV modules.

10.1. Cd production

Cadmium is produced primarily as a byproduct of zinc production. Because Zn is generated in very large quantities, there are substantial amounts of cadmium generated as byproduct. Then, no matter how much Cd is used in PV, the excess can either be put to *beneficial* uses or *discharged* into the environment. When the market does not absorb the Cd generated by metal smelters/refiners, it is cemented

and buried, stored for future use, or disposed of to landfills as hazardous waste. Arguably, encapsulating cadmium as CdTe in PV modules presents a safer option than its current uses and is much preferred to its disposal.

10.2. CdTe PV manufacturing

The two leading methods of making CdTe thin films—electrodeposition and vapor transport—use cadmium very efficiently. About 1% is wasted in the electrodeposition process, and about 10–30% is wasted in the vapor-transport process. In both processes, the cadmium can be collected and can be safely disposed of or recycled.

10.3. CdTe PV use

No emissions of any kind can be generated when using PV modules under normal conditions and during foreseeable accidents (e.g. fires, breakage). New studies proved that CdTe in glass–glass modules would not be released during fires because Cd dissolves into the molten glass and is retained there. Any comparisons made with cadmium emissions from modern coal-fired power plants are erroneous because they compare unlikely potential accidental emissions from PV systems to routine (unavoidable) emissions from conventional power plants. In reality, when PV replaces coal burning for electricity generation, it will prevent Cd emissions as well as large quantities of CO_2, NO_x, and particulate emissions. By comparison with Ni–Cd batteries, a CdTe PV module uses Cd about 2500 times more efficiently in producing electricity. A 1 KW CdTe PV system contains less cadmium than 10 size-C Ni–Cd batteries. Furthermore, CdTe is more stable and less soluble than the cadmium components used in batteries.

10.4. CdTe PV decommissioning

Releases to the aquatic environment could occur after decommissioning only if such modules end up in municipal landfills and the materials leach out. However, cadmium telluride is encapsulated between two sheets of glass and is unlikely to leach to the environment under normal conditions. No atmospheric emissions of Cd can occur under any foreseeable conditions. The PV industry is considering recycling of these modules at the end of their useful life; this would completely resolve any environmental concerns.

In summary, the environmental risks from CdTe PV are minimal. The estimated atmospheric emissions of 0.02 g of Cd per GWh of electricity produced during all the phases of the modules' life, are extremely low. Large-scale use of CdTe PV modules does not present any risks to health and the environment, and recycling the modules at the end of their useful life completely resolves any environmental concerns. During their operation, these modules do not produce any pollutants, and, furthermore, by displacing fossil fuels, they offer great environmental benefits. CdTe in PV appears to be more environmentally friendly than all other current uses of Cd, including Ni–Cd batteries.

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